[Document Name] Specification

[Title of the Invention] PHOSPHOR AND METHOD OF PRODUCING SAME

[Scope of Claims for Patent]

[Claim 1] An alkaline earth metal aluminate phosphor containing bivalent europium as an activator,

which is obtained by a process comprising;

a step (1) of firing, in a reducing atmosphere, a mixture of precursor compounds of barium and/or strontium(a), magnesium(b), aluminum(c), europium(d) and at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead, respectively, and

a step (2) of further firing, in an oxidizing atmosphere, the fired product obtained in the step (1).

[Claim 2] The alkaline earth metal aluminate phosphor according to Claim 1,

which has a powder whiteness of not lower than 85 as expressed in terms of W value.

[Claim 3] The alkaline earth metal aluminate phosphor according to Claim 1 or 2,

which further comprises 0.0001 to 0.01 mole of at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead per mole of the aluminum element

[Claim 4] The alkaline earth metal aluminate phosphor according to any one of Claims 1 to 3,

wherein the alkaline earth metal aluminate phosphor containing bivalent europium as an activator is represented by the following general formula (1):

$$(Ba_{1-X}Sr_X)_{1-Y}Eu_YMgAl_{10}O_{17} \qquad (1)$$

wherein, X satisfies the relationship of $0 \le X \le 0.3$ and Y satisfies the relationship of $0 < Y \le 0.2$.

[Claim 5] A method of producing alkaline earth metal aluminate phosphors containing bivalent europium as an activator,

which comprises a step (1) of firing, in a reducing atmosphere, a mixture of precursor compounds of barium and/or strontium(a), magnesium(b), aluminum(c), europium(d) and at least one element(e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead, respectively, and

a step (2) of further firing, in an oxidizing atmosphere, the fired product obtained in the step (1).

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to an alkaline earth metal aluminate phosphor and a method of producing the same.

[0002]

[Background Art]

In recent years, various phosphors have been used in plasma display panels (hereinafter referred to as PDPs). Among such phosphors, alkaline earth metal aluminate phosphors containing bivalent europium as an activator, for example $(Ba,Sr)MgAl_{10}O_{17}:Eu^{2+}$, are used as blue phosphors.

[0003]

When exposed to elevated temperatures or to vacuum ultraviolet rays, ultraviolet rays or the like for phosphor excitation, such alkaline earth metal aluminate phosphors containing bivalent europium as an activator deteriorate and decrease in luminance. The mechanism so far proposed as the cause therefor consists in the oxidation of bivalent Eu, which forms luminescence centers in the blue phosphors, in particular, to the trivalent form due to the oxidative effect of heating on the phosphor surface, resulting in the loss of bivalent blue luminescence centers and the decrease in luminance.

[0004]

In particular, the phosphors may be subjected to heating at elevated temperatures in the step of molding for use in certain fields of application, and therefore, it would be problematic. In the process of manufacturing PDPs, for instance, partitions called ribs are formed on the back face glass sheet, and the respective fluorescence substances each in the form of a paste prepared by using a binder and a solvent are applied to respective partition-surrounded areas without color mixing. The glass sheet is then heated at 400 to 500°C for binder elimination in the manner of firing and for fusion bonding to a front face glass sheet. It is suggested that, in such a firing step, the firing is carried out in a high humidity environment as a result of not only the oxidative action but also the evaporation of the moisture originally contained in dielectrics, electrodes and other materials than the phosphors, possibly affecting the fluorescent materials. Therefore, as far as blue phosphors are concerned, it is a great subject to inhibit luminance decreases as well as emission shifting in the heating/firing step.

[0005]

Some attempts have already been made to prevent the deterioration by chemical treatment of the phosphor surface (e.g. Patent document 1, Patent document 2, and Patent document 3). However, these methods consist in coating the surface with boric acid or a compound of such an element as antimony or silica and thereby preventing luminance decreases. Therefore, it is difficult to entirely prevent the oxidative deterioration.

[0006]

Another problem is that a phosphor, once colored and reduced in powder whiteness, absorbs the fluorescence emitted, resulting in reduced function. Therefore, it is desirable that the phosphor has high powder whiteness. As means for preventing the luminance of a phosphor from decreasing, there has been disclosed a method of producing phosphors which comprises

firing in a reducing atmosphere, followed by firing in an oxidizing atmosphere (e.g. Patent document 4). Such method, however, is a method of producing alkaline earth metal silicoaluminate phosphors but is not intended for increasing the powder whiteness of a phosphor.

[0007]

[Patent Document 1] JP-10-195428 A

[Patent Document 2] JP-10-298548 A

[Patent Document 3] JP-10-204429 A

[Patent Document 4] JP-2002-348570 A

[0008]

[Problem to be solved by the invention]

In view of the foregoing, it is an object of the present invention to provide an alkaline earth metal aluminate phosphor that does not cause luminance decreases and emission shifting but have good heat resistance durability against vacuum ultraviolet rays and ultraviolet rays, and high powder whiteness. It is another object of the present invention to provide a method of producing the same.

[0009]

[Means for solving the Problem]

The present invention relates to an alkaline earth metal aluminate phosphor containing bivalent europium as an activator, which is obtained by a process comprising:

the step (1) of firing, in a reducing atmosphere, a mixture of precursor compounds of barium and/or strontium(a), magnesium(b), aluminum(c), europium(d) and at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead, respectively, and

the step (2) of firing, in an oxidizing atmosphere, the fired product obtained in the step (1).

Preferably, the above-mentioned alkaline earth metal aluminate phosphor has a powder whiteness of not lower than 85 as expressed in terms of W value.

In the above-mentioned alkaline earth metal aluminate phosphor, the content of at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead is preferably within the range of 0.0001 to 0.01 mole per mole of the aluminum element.

[0010]

The above-mentioned alkaline earth metal aluminate phosphor containing bivalent europium as an activator is preferably represented by the following general formula (1):

$$(Ba_{1-X}Sr_X)_{1-Y}Eu_YMgAl_{10}O_{17} \qquad (1)$$

in the formula, X satisfies the relationship of $0 \le X \le 0.3$ and Y satisfies the relationship of $0 < Y \le 0.2$.

The present invention also relates to a method of producing alkaline earth metal aluminate phosphors,

which comprises a step (1) of firing, in a reducing atmosphere, a mixture of precursor compounds of barium and/or strontium(a), magnesium(b), aluminum(c), europium(d) and at least one element(e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead, respectively, or a fired product of said mixture, and

a step (2) of further firing, in an oxidizing atmosphere, the fired product obtained in the above step (1).

In the following, the present invention is described in detail.

[0011]

The fluorescent substance of the invention is an alkaline earth metal aluminate phosphor containing bivalent europium as an activator. Usable as the base fluorescent substance are generally known ones, and there may be mentioned, for example, alkaline earth metal aluminate phosphors comprising barium and/or strontium, europium, magnesium, aluminum and oxygen. Preferred as such alkaline earth metal aluminate phosphors are those represented by the following general formula (1):

$$(Ba_{1-X}Sr_X)_{1-Y}Eu_YMgAl_{10}O_{17} \qquad (1)$$

in the formula, X satisfies the relationship of $0 \leq X \leq 0.3$ and Y satisfies the relationship of $0 < Y \leq 0.2$.

[0012]

The alkaline earth metal aluminate phosphor of the invention is an alkaline earth metal aluminate phosphor containing bivalent europium as an activator and contains at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead. The element (e) may occur either within the alkaline earth metal aluminate phosphor or on the surface in a localized manner, such as resulting from surface treatment with a compound of that element. Preferably, however, it occurs within the alkaline earth metal aluminate phosphor. The fluorescent substance may contain two or more element (e) species simultaneously or contain only one element (e) species. Among the elements enumerated above, tungsten, niobium and bismuth are preferred, since they give fluorescent substances having good heat resistance and durability against vacuum ultraviolet rays and ultraviolet rays, among others; and tungsten is most preferred.

[0013]

The content of the at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead in the alkaline earth metal aluminate phosphor of the invention is preferably within the range of 0.0001 to 0.01 mole per mole of the aluminum element. At levels lower than 0.0001 mole, the effects of the addition will be little and, at levels exceeding 0.01 mole, the luminance will unfavorably become excessively low. The content level range differs depending on the element species employed. In the case of tungsten and/or niobium, for instance, a preferred lower limit to the above range is 0.0003 mole, and a preferred upper range is 0.007 mole. Further, a most preferred lower limit to the above range is 0.0005 mole, and a most preferred upper limit is 0.003 mole. The content of the above element

can be adjusted to a level within a specific range by adjusting the mixing ratio between the precursor compound of aluminum and the precursor compound of the above-mentioned element in the mixture of the precursor compounds used as the starting materials.

[0014]

The alkaline earth metal aluminate phosphor of the invention may further contain one or more elements other than the above element at levels at which they will never adversely affect the physical properties of the fluorescent substance. Since, however, the presence of an impurity may influence the luminance, heat resistance, durability against vacuum ultraviolet ray and so forth, the content of elements other than the essential components should preferably be lower than 1%.

[0015]

In the following, alkaline earth metal aluminate phosphors of the invention is described according to the method for producing them.

The alkaline earth metal aluminate phosphor of the invention can be obtained by the step (1) of firing, in a reducing atmosphere, a mixture of precursor compounds of the respective elements (barium and/or strontium (a), magnesium (b), aluminum (c), europium (d) and at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead), which are the main constituents of the alkaline earth metal aluminate phosphor, or the fired product of such mixture, and the step (2) of further firing, in an oxidizing atmosphere, the fired product obtained in the above step (1).

[0016]

The precursor compounds are not particularly restricted but each may be an oxide or any of compounds capable of being converted to oxides upon firing.

[0017]

The precursor compound of barium is not particularly

restricted but includes, for example, barium oxide, barium carbonate, barium nitrate, barium sulfate, barium sulfide, barium chloride and barium hydroxide. The precursor compound of strontium is not particularly restricted but includes, for example, strontium oxide, strontium carbonate, strontium nitrate, strontium sulfate, strontium sulfide, strontium chloride and strontium hydroxide. The precursor compound of magnesium is not particularly restricted but includes, for example, magnesium oxide, basic magnesium carbonate and magnesium hydroxide. The precursor compound of aluminum is not particularly restricted but includes, for example, aluminum oxide, aluminum nitrate, aluminum sulfate and aluminum chloride. The precursor compound of europium is not particularly restricted but includes, for example, europium oxide, europium carbonate, europium chloride and europium acetate. The oxidation number of the metal element is not particularly restricted, either.

[0018]

The precursor compound of indium is not particularly restricted but includes, for example, indium oxide, indium trichloride, indium nitrate, indium hydroxide and indium sulfate. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of tungsten is not particularly restricted but includes, for example, tungsten oxide, ammonium tungstate and tungsten hexachloride. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of niobium is not particularly restricted but includes, for example, niobium oxide and niobium pentoxide. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of bismuth is not particularly restricted but includes, for example, bismuth oxide and bismuth nitrate. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of molybdenum is not particularly restricted but includes, for

example, molybdenum oxide, ammonium molybdate and molybdenum chloride. The oxidation number of the metal element is not particularly restricted, either.

[0019]

The precursor compound of tantalum is not particularly restricted but includes, for example, tantalum oxide, tantalum chloride and tantalum fluoride. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of thallium is not particularly restricted but includes, for example, thallium oxide, thallium carbonate and thallium nitrate. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of lead is not particularly restricted but includes, for example, lead oxide, lead carbonate and lead nitrate. The oxidation number of the metal element is not particularly restricted, either.

[0020]

The compounds to be used as the precursor compounds each preferably has a purity as high as possible and, in particular, is preferably free of any impurity other than the volatile constituents or contains only a slight amount of such an impurity. If such an impurity is present in a starting material, the physical properties of the product alkaline earth metal aluminate phosphor may unfavorably be modified. It is preferable that each starting material have a purity of 99% or higher. The above-mentioned respective precursor compounds are blended together, to give a mixture, in such proportions that they give the proportions of the respective elements in the alkaline earth metal aluminate phosphor to be produced.

[0021]

In producing the alkaline earth metal aluminate phosphor of the invention, a flux may further be used. The flux is not particularly restricted but is preferably one capable of functioning as a fluorescent substance particle growth promoter and volatilizing without influencing the composition of the

fluorescent substance, for example magnesium fluoride or aluminum fluoride.

[0022]

The mixture of the precursor compounds, if necessary further containing the flux, can be prepared mixing together the respective components mentioned above by any of the conventional methods.

The method of mixing is not particularly restricted but may be any of those capable of causing homogeneous mixing without allowing aggregation of each individual component. More specifically, there may be mentioned, for example, the dry mixing method using a ball mill or blender, for instance; the method comprising wet mixing in the presence of a solvent using a homogenizer or a like agitator, a ball mill, a bead mill or a like media grinder, followed by drying; the method comprising preparing an aqueous solution of precursor compounds each in a water-soluble salt form, precipitating the precursor each in an insoluble salt form by pH adjustment with a pH adjusting agent so as to give a predetermined composition, washing the precipitate and drying the same; and the method comprising preparing an aqueous solution of precursor compounds each in a water-soluble salt form, then preparing a W/O type emulsion using the solution and an oil, together with a dispersant, heating and dehydrating the emulsion and recovering the resulting oleaginous dispersion of the precursor mixture.

[0023]

The step (1) in the present invention is a step for firing the above mixture in a reducing atmosphere.

The firing in a reducing atmosphere is preferably carried out at a temperature within the range of 1000 to 1700°C. When the firing temperature is lower than 1000°C, the fluorescence center europium is not sufficiently reduced, and luminance of the fluorescent substance becomes poor. On the contrary, temperatures higher than 1700°C may give excessively large particles and cause marked deteriorations in performance

characteristics, unfavorably making particle dispersion difficult due to strong intercrystalline fusion bonding and thus markedly inhibiting uniform fluorescent film formation. The above-mentioned firing is required to be carried out in a reducing atmosphere so that the fluorescence center europium may be reduced.

[0024]

The reducing atmosphere conditions are not particularly restricted but the firing is carried out, for example, in a nitrogen-hydrogen mixed gas atmosphere. In the firing in a nitrogen-hydrogen mixed gas atmosphere, the mixing ratio of nitrogen to hydrogen is preferably 99.9/0.1 to 80/20 (by volume).

[0025]

The reaction time in the firing in a reducing atmosphere varies depending on the reaction temperature and, for the reaction to proceed satisfactorily, a reaction time of 0.5 to 10 hours, for instance, is employed, whereupon the desired fired product can be obtained with great efficiency.

[0026]

The step (2) in the present invention is a step for further firing, in an oxidizing atmosphere, the fired product obtained in the step (1). Firing in an oxidizing atmosphere after the firing step in a reducing atmosphere enhances powder whiteness of obtained fluorescent substances, as mentioned above.

[0027]

The alkaline earth metal aluminate phosphor in the invention shows improved luminance maintaining performance as a result of addition of at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead. However, when the firing in a reducing atmosphere is carried out in the presence of such an element added, the above element is reduced, resulting in coloration or an increase in coloration. Namely, in a reducing atmosphere, the element (e) is converted to a

highly coloring lower valence substance, which reduces the powder whiteness of the fluorescent substance and lowers the luminance as a result through absorption of the light emitted. Therefore, it is necessary to further increase the powder whiteness by carrying out the above-mentioned step (2).

[0028]

Thus, owing to its containing the element (e) and, further, when prepared by the firing in an oxidizing atmosphere as the last step, the alkaline earth metal aluminate phosphor of the invention can become a fluorescent substance high in powder whiteness and durable against heating in the production process and irradiation with ultraviolet rays, vacuum ultraviolet rays, etc.

[0029]

The above-mentioned firing in an oxidizing atmosphere is not particularly restricted but mention may be made of the firing in the ambient atmosphere or in a nitrogen-oxygen mixed gas atmosphere, for instance. The firing in a nitrogen-oxygen mixed gas atmosphere is preferred among others since the oxidation of europium functioning as an activator can then be prevented as far as possible. The mixing ratio between nitrogen and oxygen in the above-mentioned mixed gas is not particularly restricted but the nitrogen/oxygen ratio is preferably 99.9/0.1 to 95/5 (by volume) so that the oxidation of europium may be inhibited.

[0030]

The nitrogen-oxygen mixed gas may retain the same mixing ratio from the initial stage to the end point of the firing. Alternatively, oxygen may be injected into the atmosphere in the course of firing if the coloration of or by the additive element can be eliminated thereby. On that occasion, the temperature, duration and time for oxygen injection are not particularly restricted but can be selected arbitrarily. The firing in an oxidizing atmosphere is preferably carried out in temperature range from the lower limit of 500°C to the upper

limit of 1000°C so that the oxidation of europium may be inhibited as far as possible. The maximum temperature, after arrival thereof, is preferably maintained for 0 to 20 hours.

[0031]

In the present invention, the above firing in an oxidizing atmosphere enhances powder whiteness of resultant alkaline earth metal aluminate phosphor.

The resultant alkaline earth metal aluminate phosphor preferably has a powder whiteness of not lower than 85 as expressed in terms of W value. The alkaline earth metal aluminate phosphor with a powder whiteness of not lower than 85 as expressed in terms of W value is preferred since it will not absorb the fluorescence emitted but can send out fluorescence efficiently. The W value is calculated from the values of L (brightness), a (chroma) and b (hue) according to Hunter's color model, by using the following formula (2):

$$W = 100 - \{(100 - L)^2 + (a^2 + b^2)\}^{1/2} \qquad (2)$$

When the W value is smaller than 85, high levels of absorption of the fluorescence emitted will result and, possibly, no good fluorescent substance performance characteristics may be acquired. More preferably, the W value is 90 or higher.

[0032]

The alkaline earth metal aluminate phosphor with a powder whiteness of not lower than 85 as expressed in terms of W value is preferred since it will not absorb the fluorescence emitted but can send out fluorescence efficiently. The powder whiteness is susceptible to various factors, such as type or amount of the element (e) to be added, firing conditions or firing time in producing process, etc. Thus, the alkaline earth metal aluminate phosphor with a powder whiteness of not lower than 85 can be obtained by controlling these ingredients or production conditions. It is possible to obtain an alkaline earth metal aluminate phosphor with a powder whiteness of not lower than 85 without conducting the above step (2). Even in such a case, the step (2) can provide high-performance

fluorescent substances with a powder higher whiteness.

[0033]

The alkaline earth metal aluminate phosphor of the invention is excellent in quality also from the viewpoint that the luminous color shifting is inhibited. The luminous color shifting so referred to herein is the change in chromaticity of the light emitted by the alkaline earth metal aluminate phosphor, and a smaller change in chromaticity of the light emitted indicates a smaller change in luminous color, hence a higher degree of inhibition of luminous color shifting. The change in chromaticity of the light emitted can be calculated using the chromaticity (y) of the light emitted by the fluorescent substance as measured by using a luminance meter (e.g. Otsuka Electronics model MCPD-3000) according to the following formula (3):

Δy = chromaticity (y2) of the light emitted after firing, ultraviolet irradiation, etc. - chromaticity (y1) of the light emitted by the fluorescent substance in powder form (3)

[0034]

For example, a fluorescent substance for which the change in chromaticity (Δy) of the light emitted between the measurement immediately after preparation and the measurement after the heating step comprising heating in the air at a rate of 150°C per hour, maintaining the temperature of 500°C for 1 hour and then cooling at a rate of 150°C per hour is smaller than 0.01 can be regarded as being inhibited from luminous color shifting. When the change exceeds 0.01, the change in luminous color is great and the luminous color shifting inhibiting performance is unsatisfactory. More preferably, the above-mentioned change in chromaticity is not greater than 0.007.

[0035]

The alkaline earth metal aluminate phosphor fired in an oxidizing atmosphere in the manner described above is preferably ground to adjust the particle diameter. Usable as

the grinder to be used in the above-mentioned grinding are dry grinders such as hammer mills, fluid energy mills and mixing mullers, and wet grinders such as ball mills and bead mills. In the above-mentioned grinding, excessively intense grinding may result in marked deteriorations in fluorescent substance characteristics and, therefore, it is necessary to select an adequate grinder or mill and employ best working conditions. The classification procedure using a liquid cyclone or the like may also be properly utilized.

[0036]

In the above-mentioned method of producing alkaline earth metal aluminate phosphors, the firing in a reducing atmosphere may be preceded by an arbitrary number of firing steps each in an arbitrary atmosphere according to need. As such firing prior to the firing in a reducing atmosphere, there may be mentioned, for example, the firing in an oxidizing atmosphere.

[0037]

As the above-mentioned optional firing in an oxidizing atmosphere, which is not particularly restricted, there may be mentioned, for example, the firing in the ambient atmosphere or in a nitrogen-oxygen mixed gas atmosphere. The optional firing in an oxidizing atmosphere is preferably carried out at a temperature of 1000 to 1700°C. The reaction time in the optional firing in an oxidizing atmosphere varies depending on the reaction temperature; for the reaction to proceed satisfactorily, a reaction time of 0.5 to 10 hours, for instance, is employed, whereupon the intended purpose can be accomplished efficiently. In cases where the firing in a reducing atmosphere is carried out after the above-mentioned firing in an arbitrary atmosphere, the firing in a reducing atmosphere is preferably carried out after appropriate grinding of the fired product in an arbitrary atmosphere.

[0038]

The alkaline earth metal aluminate phosphor of the invention is excellent in heat resistance and in durability

against vacuum ultraviolet rays or ultraviolet rays, and shows no luminance reduction or luminous color shifting, hence can be properly used in PDPs and in like applications. Furthermore, the above alkaline earth metal aluminate phosphor shows a high powder whiteness and therefore is excellent in fluorescence-emitting capacity. The above method of producing alkaline earth metal aluminate constitutes one aspect of the present invention.

[0039]

[Examples]

The following examples further illustrate the present invention. They are, however, by no means limitative of the scope of the invention.

(Example 1)

Using an electronic force balance, 24.11 g of barium carbonate (purity on analysis: 99.39% by weight), 2.1 g of strontium carbonate (purity on analysis: 99.5% by weight), 8.33 g of magnesium hydroxide (purity on analysis: 99.5% by weight), 73.32 g of aluminum oxide (purity on analysis: 99.27% by weight), 1.26 g of europium(III) oxide (99.6% by weight), 0.198 g of indium(III) oxide (special reagent grade) and 1.19 g of aluminum fluoride (special reagent grade) were weighed respectively, and they were mixed up in an automatic mortar (product of Nitto Kagaku Co., ANM-150) for 60 minutes. The mixture was then placed in an alumina crucible and fired in the ambient atmosphere by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. Then, the fired product was subjected to reductive firing, in an electric oven maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen and 90% by volume of nitrogen, by raising the temperature at

a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. The fired product was further fired in an electric oven maintained in an oxidizing atmosphere with a mixed gas composed of 10% by volume of oxygen and 90% by volume of nitrogen by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 800°C, maintaining that temperature for 1 hour, followed by cooling at a rate of 200°C per hour. The thus-obtained fired product was pulverized in an automatic mortar for 5 minutes.

In the above manner, there was obtained an alkaline earth metal aluminate phosphor (A) containing indium in an amount of 0.001 mole as the element In per mole of the aluminum element.

[0040]

(Example 2)

An alkaline earth metal aluminate phosphor (B) containing tungsten in an amount of 0.001 mole as the element W per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.331 g of tungsten(VI) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0041]

(Example 3)

An alkaline earth metal aluminate phosphor (C) containing niobium in an amount of 0.001 mole as the element Nb per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.190 g of niobium(V) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0042]

(Example 4)

An alkaline earth metal aluminate phosphor (D) containing bismuth in an amount of 0.001 mole as the element Bi per mole

of the aluminum element was obtained in the same manner as in Example 1 except that 0.333 g of bismuth(III) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0043]

(Example 5)

An alkaline earth metal aluminate phosphor (E) containing molybdenum in an amount of 0.001 mole as the element Mo per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.206 g of molybdenum(VI) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0044]

(Example 6)

An alkaline earth metal aluminate phosphor (F) containing tantalum in an amount of 0.001 mole as the element Ta per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.315 g of tantalum(V) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0045]

(Example 7)

An alkaline earth metal aluminate phosphor (G) containing thallium in an amount of 0.001 mole as the element Tl per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.326 g of thallium(III) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0046]

(Example 8)

An alkaline earth metal aluminate phosphor (H) containing bismuth in an amount of 0.001 mole as the element Pb per mole of the aluminum element was obtained in the same manner as in Example 6 except that 0.319 g of lead(II) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III)

oxide (special reagent grade).

[0047]

(Comparative Example 1)

Using an electronic force balance, 24.11 g of barium carbonate (purity on analysis: 99.39% by weight), 2.1 g of strontium carbonate (purity on analysis: 99.5% by weight), 8.33 g of magnesium hydroxide (purity on analysis: 99.5% by weight), 73.32 g of aluminum oxide (purity on analysis: 99.27% by weight), 1.26 g of europium(III) oxide (99.6% by weight), 0.198 g of indium(III) oxide (special reagent grade) and 1.19 g of aluminum fluoride (special reagent grade) were weighed respectively, and they were mixed up in an automatic mortar (product of Nitto Kagaku Co., ANM-150) for 60 minutes. The mixture was then placed in an alumina crucible and fired in the ambient atmosphere by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. Then, the fired product was subjected to reductive firing, in an electric oven maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen and 90% by volume of nitrogen, by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. In the above manner, an alkaline earth metal aluminate phosphor (I) that contained indium in an amount of 0.001 mole as the element In per mole of aluminum element, but did not fired in any oxidizing atmosphere.

[0048]

(Comparative Example 2)

An alkaline earth metal aluminate phosphor (J) containing tungsten in an amount of 0.001 mole as the element W per mole

of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.331 g of tungsten(VI) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0049]

(Comparative Example 3)

An alkaline earth metal aluminate phosphor (K) containing niobium in an amount of 0.001 mole as the element Nb per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.190 g of niobium(V) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0050]

(Comparative Example 4)

An alkaline earth metal aluminate phosphor (L) containing bismuth in an amount of 0.001 mole as the element Bi per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.333 g of bismuth(III) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0051]

(Comparative Example 5)

An alkaline earth metal aluminate phosphor (M) containing molybdenum in an amount of 0.001 mole as the element Mo per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.206 g of molybdenum(VI) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0052]

(Comparative Example 6)

An alkaline earth metal aluminate phosphor (N) containing tantalum in an amount of 0.001 mole as the element Ta per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.315 g of tantalum(V) oxide (special reagent grade) was added in lieu of the addition of

0.198 g of indium(III) oxide (special reagent grade).

[0053]

(Comparative Example 7)

An alkaline earth metal aluminate phosphor (O) containing thallium in an amount of 0.001 mole as the element Tl per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.326 g of thallium(III) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0054]

(Comparative Example 8)

An alkaline earth metal aluminate phosphor (P) containing lead in an amount of 0.001 mole as the element Pb per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.319 g of lead(II) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0055]

(Method of powder whiteness measurement)

Each of the alkaline earth metal aluminate phosphors obtained in Examples 1 to 8 and Comparative Examples 1 to 8 was packed in a vessel with a diameter of 10 mm and a depth of 5 mm and, after smoothening the surface, the Hunter color model L, a and b values were measured using a color meter (product of Suga Test Instruments; trademark: SM Color Computer, SM-4) and the W value was calculated. The results thus obtained are shown in Table 1.

[0056]

[Table 1]

		Element added	Oxidative firing	L	a	b	W
Examples	1	In	Done	91.3	−0.11	−3.05	90.7
	2	W	Done	95.2	0.22	−3	94.3
	3	Nb	Done	95.1	−0.07	−3.03	94.2
	4	Bi	Done	89.1	−0.05	−2.45	88.8
	5	Mo	Done	92.3	0.21	−2.98	91.7
	6	Ta	Done	94.7	0.28	−3.19	93.8
	7	Tl	Done	90.9	−0.10	−2.88	90.5
	8	Pb	Done	94.6	0.22	−3.01	93.8
Comparative Examples	1	In	Not done	88.7	−0.34	−4.49	87.8
	2	W	Not done	87.6	0.15	−1.40	87.5
	3	Nb	Not done	91.9	−0.57	−3.87	91.0
	4	Bi	Not done	70.6	0.65	−1.38	70.5
	5	Mo	Not done	86.8	0.11	−1.60	86.7
	6	Ta	Not done	74.6	1.87	−0.99	74.5
	7	Tl	Not done	85.8	−0.43	−5.51	84.8
	8	Pb	Not done	93.0	0.55	−4.06	91.9

Table 1 indicates that the phosphors of Examples 1 to 8 which had been subjected to firing in an oxidizing atmosphere as the last step were higher in powder whiteness than the comparative phosphors containing the respective same additive elements but not subjected to firing in any oxidizing atmosphere.

[0058]

(Comparative Example 9)

An alkaline earth metal aluminate phosphor (Q) was obtained in the same manner as in Example 1 except that the addition of 0.198 g of indium oxide was omitted.

[0059]

(Comparative Example 10)

Using an electronic force balance, 24.11 g of barium carbonate (purity on analysis: 99.39% by weight), 2.1 g of strontium carbonate (purity on analysis: 99.5% by weight), 8.33

g of magnesium hydroxide (purity on analysis: 99.5% by weight), 73.32 g of aluminum oxide (purity on analysis: 99.27% by weight), 1.26 g of europium oxide (purity on analysis: 99.6% by weight), and 1.19 g of aluminum fluoride (special reagent grade) were weighed respectively, and they were mixed up in an automatic mortar (product of Nitto Kagaku Co., ANM-150) for 60 minutes. The mixture was then placed in an alumina crucible and fired in the ambient atmosphere by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. Then, the fired product was subjected to reductive firing, in an electric oven maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen and 90% by volume of nitrogen, by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. In the above manner, there was obtained an alkaline earth metal aluminate phosphor (R) that did not contain any additional element and did not fired in an oxidizing atmosphere.

[0060]

(Method for testing heat resistance and method of deterioration testing by vacuum ultraviolet irradiation)

The phosphors obtained in Examples 1 to 8 and Comparative Examples 9 and 10 were subjected to powder luminance measurement and to deterioration testing by vacuum ultraviolet irradiation. Prior to testing, test specimens were first prepared from the powder-form phosphors themselves as obtained in Examples 1 to 8 and Comparative Examples 9 and 10 in the same manner as in the powder whiteness measurement, and the emissive luminance and emissive chromaticity (y value) of each specimen were

measured using an Otsuka Electronics model MCPD-3000 luminance meter. Then, test specimens for ultraviolet irradiation were prepared as follows:

Each of the alkaline earth metal aluminate phosphors obtained in the examples 1 to 8 and comparative example 9 and 10 was mixed with ethylcellulose (product of Dow Chemical, STD-10) and terpineol (special reagent grade) in a ratio of 17.5:1:9 on the weight basis, and the mixture was dispersed on a Hoover muller to give a phosphor paste. Each phosphor paste was applied onto a slide glass to give a 2 x 2 cm film with a dry film thickness of 20 µm, and the film was fired in the air at 500°C for 20 minutes to remove the binder and solvent components.

The thus-obtained fired films were used as test specimens. At first, luminance and chromaticity (y value) were measured, and then each test specimen was irradiated with ultraviolet rays at 147 nm under vacuum (≤ 5 Pa) for 2 hours using a vacuum ultraviolet lamp (product of Ushio Inc.).

[0061]

The difference (emissive chromaticity (y value) of the fired film) - (emissive chromaticity (y value) in powder form) was defined as change in chromaticity (Δy), and the changes were compared. Further, luminance measurements were carried out before and after vacuum ultraviolet irradiation, and the value (luminance after irradiation)/(luminance before irradiation) x 100, which was defined as luminance retention percentage, was calculated for each phosphor, and the extents of deterioration of the respective samples before and after firing were compared based on the luminance retention percentage values obtained. The results are shown in Table 2. The luminance values shown in Table 2 are relative luminance values converted from the measured luminance values in the respective tests taking the measured luminance value of the powder of Comparative Example 9 as 100.

[0062]

[Table 5]

		Element added	Oxidative firing	Powder luminance	Film luminance	After vacuum UV irradiation	Luminance retention	Change in chromaticity
Example	1	In	Done	105	103	95	92	0.002
	2	W	Done	114	114	108	95	0.000
	3	Nb	Done	110	108	105	97	0.001
	4	Bi	Done	102	100	93	93	0.003
	5	Mo	Done	104	100	93	93	0.002
	6	Ta	Done	102	98	90	92	0.002
	7	Tl	Done	103	99	92	93	0.003
	8	Pb	Done	105	100	92	92	0.004
Comparative Example	9	-	Done	100	97	86	89	0.006
	10	-	Not done	115	116	96	83	0.031

[0063]

The results shown in Table 2 indicate that the tungsten-containing phosphor of Example 2 and the niobium-containing phosphor of Example 3, in particular, showed increases, by 10% or more, in luminance after vacuum ultraviolet irradiation as compared with the phosphors of Comparative Examples 9 and 10, which indicates marked prevention of deterioration by vacuum ultraviolet rays.

It was also shown that the luminance was high but the luminous color shifting was great in Comparative Example 10 whereas the phosphors of Examples 1 to 8 showed very slight changes in emission chromaticity, indicating the prevention of luminous color shifting.

[0064]

[Effect of the invention]

The alkaline earth metal aluminate phosphor of the invention is a phosphor excellent in luminance retention performance with the deterioration with time and the luminous color shifting upon heating and vacuum ultraviolet irradiation being markedly suppressed. Furthermore, the alkaline earth metal aluminate phosphor of the invention is a phosphor showing a high powder whiteness and excellent in fluorescence reflecting properties.

[Document Name] Abstract

[Abstract]

[Subject] To provide an alkaline earth metal aluminate phosphor that does not cause luminance decreases and emission shifting but have good heat resistance durability against vacuum ultraviolet rays and ultraviolet rays, and high powder whiteness, and a method of producing the same.

[Means for solving] An alkaline earth metal aluminate phosphor containing bivalent europium as an activator, which is obtained by a process comprising; a step (1) of firing, in a reducing atmosphere, a mixture of precursor compounds of barium and/or strontium(a), magnesium(b), aluminum(c), europium(d) and at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead, respectively, and a step (2) of further firing, in an oxidizing atmosphere, the fired product obtained in the step (1).

[Selective Figure] None